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(71) Applicant(s)
Sandoz Ltd

(Incorporated in Switzerland)

35 Lichtstrasse, CH-4002 Basle, Switzerland

(72) Inventor(s)
Peter Staniek
Klaus Stoll
Rainer Wolf

(74) Agent and/or Address for Service
B A Yorke & Co
Coomb House, 7 St John's Road, Isleworth,
Middlesex, TW7 6NH, United Kingdom

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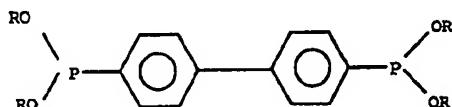
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(56) Documents Cited
GB 2278362 A GB 2261667 A GB 2260764 A
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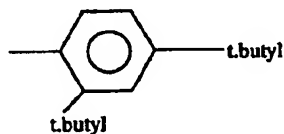
(58) Field of Search
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(54) Processing stabilizers for polymers

(57) A polymeric composition comprises polymer prepared with a Generation II to V catalyst and a compound of formula I



in which each R is

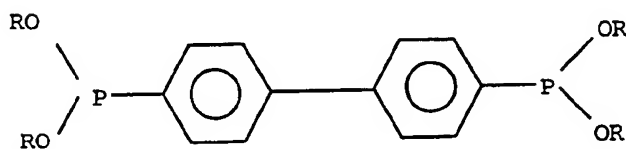


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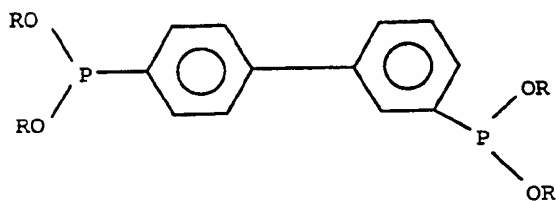
PROCESSING STABILISERS

SANDOSTAB P-EPQ, a processing stabilizer and nucleating agent for use in polymers.

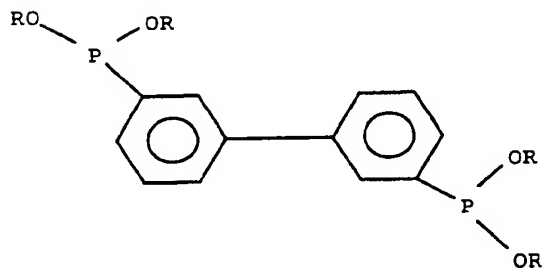
Sandostab P-EPQ is an excellent antioxidant and is a mixture of the following five compounds of formula I-V below



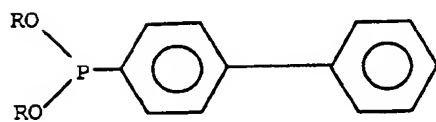
I 36-46%



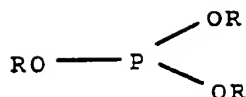
II 17-23%



III 2-5%

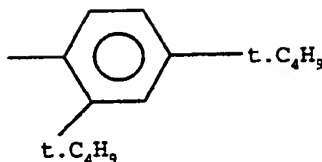


IV 11-19% and



V 9-18%

where each R is



SANDOSTAB P-EPQ can be added in amounts from 0.02-5%, preferably 0.02-2% based on the weight of polymer to which it is added.

Polymeric materials that can be stabilized by SANDOSTAB P-EPQ include homopolymers, copolymers and polymer blends of:

Cellulose acetate; Cellulose acetobutyrate; Cellulose acetopropionate; Cresol-formaldehyde resin; Carboxymethylcellulose; Cellulose nitrate; Cellulose propionate; Casein plastics; Casein-formaldehyde; Cellulose triacetate; Ethyl cellulose; Epoxy resins; Methyl cellulose; Melamine-formaldehyde resins; Polyamide; Polyamideimide; Polyacrylonitrile; Polybutene-1 and -2; Polybutylacrylate; Poly- (butylene-terephthalate); Polycarbonate; Poly(chloro trifluoroethylene); Poly(diallyl-phthalate); Polyethylene; chlorinated Polyethylene; Polyketone; Poly(etherketone); Polyetheretherketones; Polyimide; Polyether-imide; Polyethyleneoxide; Polyethersulphone; Poly(ethyleneterephthalate); Polytetra-fluoroethylene; Phenolformaldehyde resins; Polyimide; Polyisobutylene; Polyiso-cyanurate; Polymethacrylimide; Polymethyl-methacrylate; Poly(4-methylpentene-1); Poly(α -methylstyrene); Polyoxymethylene; Poly-formaldehyde; Polyacetal; Poly-propylene; Polyphenylene ether; Polyphenylenesulphide; Polyphenylenesulphone; Polystyrene; Polysulphone; Polyurethane; Polyvinyl acetate; Polyvinyl alcohol; Polyvinylbutyral; chlorinated Polyvinyl chloride; Polyvinylidene chloride; Polyvinylidene fluoride; Polyvinylfluoride; Polyvinylformaldehyde; Polyvinylcarbazol; Polyvinyl-pyrrolidone; Silicon polymers; saturated polyester; urea-formaldehyde resins; unsaturated polyester; polyacrylate; polymethacrylate; polyacrylamide; maleinate resins;

phenolic resins; aniline resins; furane resins; acrylic and polyester adhesive compositions; polyvinylcarbazole; polysulphone; epoxy-hybrids; carbamide resins; epoxide resins and silicon resins.

Examples of suitable copolymers include:

Acrylonitrile/butadiene/acrylate; Acrylonitrile/butadiene/styrene; Acrylonitrile/methylmethacrylate; Acrylonitrile/styrene/acrylic ester; Acrylonitrile/ethylenepropylene-diene/styrene; Acrylonitrile/chlorinated polyethylene/styrene; Ethylene/ethylacrylate; Ethylene methacrylic acid ester; Ethylene/propylene; Ethylene/propylenediene; Ethylene/vinyl acetate; Ethylene/vinyl alcohol; Ethylene/tetrafluoroethylene; Tetra-fluoroethylene/hexafluoropropylene; Methacrylate/butadiene/styrene; Melamine/phenol formaldehyde; Polyester blockamide; Perfluoroalkoxyalkane; Styrene/acrylonitrile; Styrene/butadiene; Styrene/maleic acid anhydride; Styrene/ α -methylstyrene; Vinyl-chloride/ethylene; Vinylchloride/ethylene/methacrylate; Vinylchloride/ethylene/vinyl acetate; Vinylchloride/methylmethacrylate; Vinylchloride/octylacrylate; Vinylchloride/ vinyl acetate; and Vinylchloride/vinylidene chloride.

Preferred polymeric materials that can be stabilized are polyolefins such as polypropylene, polyethylene (e.g. high density polyethylene, low density polyethylene, linear low density polyethylene or medium density polyethylene), polybutylene, poly-4-methylpentene and copolymers thereof as well as polycarbonate, polystyrene and polyurethane.

Preferred polyurethanes are those prepared from isocyanate resins and polyols. Preferred isocyanates are those commercially available as Desmodur, Elastan, Lupranat, Tedimon, Scuranat, Suprasec, Systanat, Hylene, Isonate (-Papi), Multrathane, Nacconate and Sumidur.

Preferred polyols are those commercially available as Desmophen, Lupranol, Lupraphen, Glendion, Napiol, Scuranol, Caradol, Daltolac, Daltorez, Diorez, Estolan, Propylan, Armol, Bermodol, Isonol, Metpol, Multron, Multranol, Niox Polyol, Pluracol, Quadrol, Thanol, Voranol and Sumiphen.

Such polyurethanes are as describes in Saechtling: Kunststoff Taschenbuch 23. Ausgabe - published by Carl Hansen Verlag 1986 (esp. p. 339-410).

Further additives (each of which, when present, is added in amount of 0.02-5%) that can be added before, after or together with, SANDOSTAB P-EPQ include further antioxidants, such as sterically hindered phenols, secondary aromatic amines or thioethers, such as described in "Kunststoff-Additive" - Gächter /Müller, Ed. 3, 1990 p.42-50, acid scavengers such as sodium-, magnesium -or calcium- stearates or -lactates, hydrotalcite or alkoxylated amines; U.V. stabilizers such as sterically hindered amines (for example N-unsubstituted, N-alkyl or N-acyl substituted 2,2,6,6-tetra-methylpiperidine compounds - also known as hindered amine light stabilizers - HALS) and U.V. absorbers (e.g. 2-(2'-hydroxyphenyl)- benzotriazoles, 2-hydroxybenzophenones, 1,3-bis-(2'-hydroxy-benzoyl)benzene salicylates, cinnamates and oxalic acid diamides), U.V. quenchers such as benzoates and substituted benzoates, antistatic agents, flameproofing agents, lubricants, plasticizers, nucleating agents, metal deactivators, biocides, impact modifiers, fillers, pigments and fungicides.

The additives mentioned in this paragraph, in particular Sandostab P-EPQ, can easily be processed into concentrates or masterbatches either as single components or as combination with one or more additional additives, which may be required for stabilization or to obtain the desired polymer properties. Preferred carriers for such concentrates or masterbatches are the same polymers, as those to be eventually stabilized (see preceding paragraphs) or polymers, which have sufficient compatibility with the matrix to which the concentrates or masterbatches are to be added, which may even show technical advantages over the use of pure additives or additive combinations. This is due to the fact that a concentrate or masterbatch is usually better and faster distributed or dispersed in the polymer than pure additives or combinations of additives. In this way, polymer degradation is further minimized owing to reduced pre-damage and more effective overall stabilization is achieved.

Sandostab P-EPQ can be particularly useful as a processing stabiliser for polyolefins and especially α - polyolefins prepared using processing catalysts known as Generation II to Generation V catalysts and which have not been subjected to a catalyst removal step. By the

term "catalyst removal step" used herein is meant a step for the purpose of positively removing the catalyst residues contained in the polymerized polyolefins or treating the polyolefins with a compound which can react with the catalyst residue and inactivate or solubilize the residue, (such as alcohols or water) and then removing the inactivated or solubilized catalyst residue by physical means such as filtration, washing and centrifuging. Thus, in the case of suspension polymerization, the step of separating the resulting polymer from a dispersion medium, such as a solvent or a liquefied monomer, does not fall under the above-mentioned definition of the catalyst residue removal step, although the catalyst dissolved in the dispersion medium may be removed by a separation step. The step of adding a small amount of catalyst poison such as ethers, alcohols, ketones, esters and water to the resulting polymer, to inactivate the catalyst remaining after the completion of polymerization, or the step of treating the resulting polymer suspension with gas such as steam or nitrogen to remove the dispersion medium does not fall under the above-mentioned definition of the "catalyst residue-removal" step.

Generation I catalysts are titanium halide catalysts and an organo aluminium compound or an organo aluminium halide.

Generation II catalysts are Generation I catalysts supported on an organo magnesium compound or based on an organo chromium compound supported on SiO_2 .

Generation III catalysts are Ziegler type complex catalysts (i.e. Generation II catalyst) supported on a halogen containing magnesium compound.

Generation IV catalysts are Generation III catalysts with a silane donor.

Generation V catalysts are a bis-indenyl organo titanium compound supported on alumoxane or bis-cyclopentadienyl titanium halides activated by aluminium alkyl compound.

Further generations of highly specific catalysts, especially useful for manufacturing highly stereoregular poly- α -olefins, which are presently under development, also belong to the

aforementioned generations of supported catalyst systems. Examples of the microstructure of such highly stereoregular polyolefins are syndiotactic polypropylene, isotactic stereoblock polymers, isotactic polypropylene containing stearic defects randomly distributed along the polymer chain (so called "anisotactic polypropylene") or stereoirregular stereoblock polymers.

Reviews of the most recent developments in the field of metallocene based catalyst systems are: W. Neissl and H. Ledwinka: *Kunststoffe* 83 (1993) 8 pages 577-583; R. Mülhaupt: *Nachr. Chem. Tech. Lab.* 41 (1993) 12 pages 1341-1351; R. D. Leaversuch: *Modern Plastics*, Oct. 1991 pages 46-49 and W. Spaleck: *Hoechst High Chem Magazine* 14 (1993) pages 44-48.

Due to the rapid progress in the development of newer generation catalyst systems, the commercial significance of these polymers with novel, highly interesting properties is increasing. However, it is expected that residues of such further generations of catalyst, so long as they contain metals of the 3d, 4d and 5d series of the Periodic Table supported analogously to the earlier catalyst generations, will also cause disadvantageous properties in the polymer, so long as such residues remain in the polymer (even in a deactivated form). Accordingly, it can be predicted and be expected that Sandostab P-EPQ will be also suitable for overcoming such disadvantageous properties of the polymer. This means that any disadvantageous interaction between processing stabilizers and the aforementioned residues of catalysts of further generations, particularly the hydrolysis of phosphites and phosphonites, will effectively be inhibited by SANDOSTAB P-EPQ.

These generations of catalysts are described in the "Twelfth Annual International Conference on Advances in the Stabilization and Controlled Degradation of Polymers" held in Luzern, Switzerland, 21-23 May 1990 in an article on pages 181 to 196 inclusive by Rolf Mülhaupt entitled "New Trends in Polyolefin Catalysts and Influence on Polymer Stability" and especially Table I on page 184 describing the Generation of Catalysts set out below.

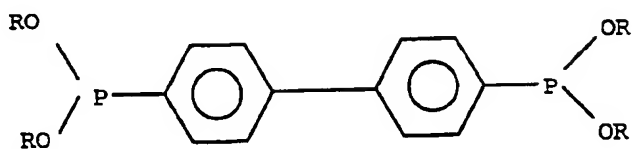
TABLE I Polyolefin Catalyst Evolution

Generation	Example	Cat.Act. % (g/PP/gTi hatm)	Act.Ti (% insol in heptane)	Stereoreg. (% insol in heptane)	Process Technology
I.	TiCl ₄ /AlR ₃	40	0.01	45%	removal of cat.residues and atactic PP
	TiCl ₃ /AlEt ₂ Cl	30	0.1	92%	removal of catalyst residues
II	Mg(OEt ₂)/TiCl ₄ /AlR ₃ SiO ₂ /Cp ₂ Cr	40000 40000	HDPE	50%	no removal of cat.residues (mainly HDPE/LLDPE)
III	Mod.TiCl ₃ cat. MgCl ₂ /TiCl ₄ /AlR ₃ +ester donor	5000 20000	1 10	95% 92%	no purification
IV	MgCl ₂ /TiCl ₄ /AlR ₃ +silane donor	40000	18	99%	no purification no extrusion
V	Bis-indenyl-TiR ₂ on (AlCH ₃ O) ₂	40000	100	99%	novel PPs, narrow MWD

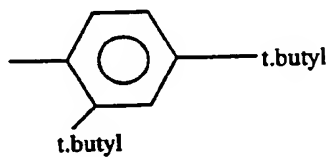
in which R is an organo group; HDPE is high density polyethylene, LLDPE is linear low density polyethylene, Cp is cyclopentadienyl, Et is ethyl, PP is polypropylene and MWD is molecular weight distribution.

CLAIMS

1. A polymeric composition comprising polymer prepared with a Generation II to V catalyst and
a compound of formula I



in which each R is



Patents Act 1977
Examiner's report to the Comptroller under Section 17
(TI Search report)

Application number
GB 9421983.9

Relevant Technical Fields

(i) UK Cl (Ed.N) C3K (KCE, KCZ)

(ii) Int Cl (Ed.6) C08K 5/5333

Search Examiner
MISS M KELMAN

Date of completion of Search
10 JANUARY 1995

Databases (see below)

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

Documents considered relevant following a search in respect of Claims :-
1

(ii)

Categories of documents

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|---|---|
| X: Document indicating lack of novelty or of inventive step. | P: Document published on or after the declared priority date but before the filing date of the present application. |
| Y: Document indicating lack of inventive step if combined with one or more other documents of the same category. | E: Patent document published on or after, but with priority date earlier than, the filing date of the present application. |
| A: Document indicating technological background and/or state of the art. | &: Member of the same patent family; corresponding document. |

Category	Identity of document and relevant passages		Relevant to claim(s)
X, E	GB 2278362 A	(SANDOZ) 30 November 1994, see pages 32 to 33	1
X	GB 2261667 A	(SANDOZ) see the example	1
X	GB 2260764 A	(SANDOZ) see page 2 line 18 to page 3 line 3, and page 11 line 12 to page 15, line 3	1
X	GB 2257706 A	(SANDOZ) see page 9 lines 2 to 6, and page 17 line 7 to page 20 line 13	1
X	US 4824885 A	(MAGNI) see examples 1 and 3	1

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).